Development of Ion Exchange Resins with Ultra Low Residuals for Condensate Polishing Applications

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Summary

- Ultra-Low Chloride (ULC) Anion Resin
  - Introduction
  - Objectives
  - Background
  - Development and Commercialization
  - Installation and Service History
  - Plant Experience
  - Iron Transport Reduction
  - Conclusions and Benefits
  - Future Installations
  - Acknowledgments

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Summary

- Ultra-Low Sulfate (ULS) Cation Resin
  - Objectives
  - Resin Candidates
  - Testing Protocol
  - Future Work
  - Conclusions
  - Acknowledgments

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Ultra Low Chloride Strong Base Anion Resins

Introduction

- Customer Driven Product Development Work
  - Dominion Millstone Power Station
  - High Purity Caustic for Anion Resin Regenerations
  - Ultra Low Residual Chloride on Strongly Basic Anion Resin

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Objectives

- Higher Purity Strongly Basic Anion Resin for Condensate Polishing Applications in PWR's
- Reduction in Release of Residual Impurities (Cl^-) from Anion Resin
- Increase in Amine (ETA) for pH Control
- Decrease in Corrosion Product (Fe) Transport

Background

- Dominion Millstone Nuclear Power Station
  - Located in Waterford, Connecticut, USA
  - 2 Operating PWR's
    - 895 MWe Unit 2
    - 1154 MWe Unit 3
  - Operation
    - ETA Based Secondary Side Chemistry
    - Full-Flow Condensate Polishing
    - Non-Molar Ratio Chemistry
    - Seawater Cooled

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Background

- Millstone Condensate Polishers
  - Traditional H^+/OH^- Operation
  - 3:2 Ratio of Anion to Cation
  - 5.7 m^3 (200 ft^3) Resin per Vessel
  - Unit 2
    - 7 Vessels
    - 8 Resin Charges
  - Unit 3
    - 8 Vessels
    - 9 Resin Charges

Background

- Minimize Feedwater Corrosion Transport
  - Increase Dissolved Oxygen Content
    - Air Injection for Unit 2 Only
  - Elevate Secondary Side pH
    - Utilize ETA Form Strong Acid Resin
    - Increase ETA Concentration
    - Decrease Chloride Concentration
      - Caustic Purity Limitation

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Development and Commercialization

- Ultra Low Chloride Strong Base Resin for Condensate Polishers
  - Residual Chloride Content
    - Conventional Low Chloride Resins –
      - <0.5 % of Sites (Condensate Grades)
      - <0.1% of Sites (Nuclear Grades
    - Ultra Low Chloride Resin –
      - <0.015% of Sites
      - <30 ng/L (ppt) of chloride Leakage

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Development and Commercialization

- Development of Novel Ultra Low Chloride Processes
  - Post-Processed Caustic
  - Ultra Low Chloride Strong Base Anion Resin (Gravex® GR 1-9 Ultra)

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Unit 2 – Installation and Service History

Lot No.	Date Installed	Service Time	Throughput	Effluent Chloride
		(days)	(X 10^9 L)	(ng / L)
GR-2164	09/02/04	1401	21.75	28
GR-2497	09/01/05	125	2.0	
GR-2579	01/11/06	905	14.0	25
GR-2579	01/21/06	114	1.8*	25
GR-2668	05/24/07	407	6.3	16
GR-3100	08/09/07	330	5.1	19

* Removed due to contamination from mechanical repairs.

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Unit 3 – Installation and Service History

Lot No.	Date Installed	Service Time	Throughput	Effluent Chloride
		(days)	(X 10^9 L)	(ng / L)
GR-2374	04/07/05	482	7.9	33
GR-2497	09/01/05	202	3.2	
GR-2668	03/29/06	531	8.3	22
GR-2668	03/30/06	171	2.3	27
GR-2668	04/14/06	812	12.6	22

Unit 3 – Installation and Service History (cont.)

Lot No.	Date Installed	Service Time	Throughput	Effluent Chloride
		(days)	(X 10^9 L)	(ng / L)
GR-3100	12/07/07	197	3.1	20
GR-3234	01/13/08	173	2.7	10
GR-3234	O3/31/08	95	1.5	8
GR-2374#	05/01/08	64	0.98	30

Regenerated after H/OH operation.

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Millstone Experience

- Ultra Low Chloride Evaluation at Dominion Millstone Power Station
  - Initial Installation (Sept. 2004)
  - Cumulative Experience
    - 7 Lots of Gravex GR 1-9 Ultra
    - 15 Vessels Installed
    - 9 Beds Operational
    - Extended Service Time
    - Extended Throughput

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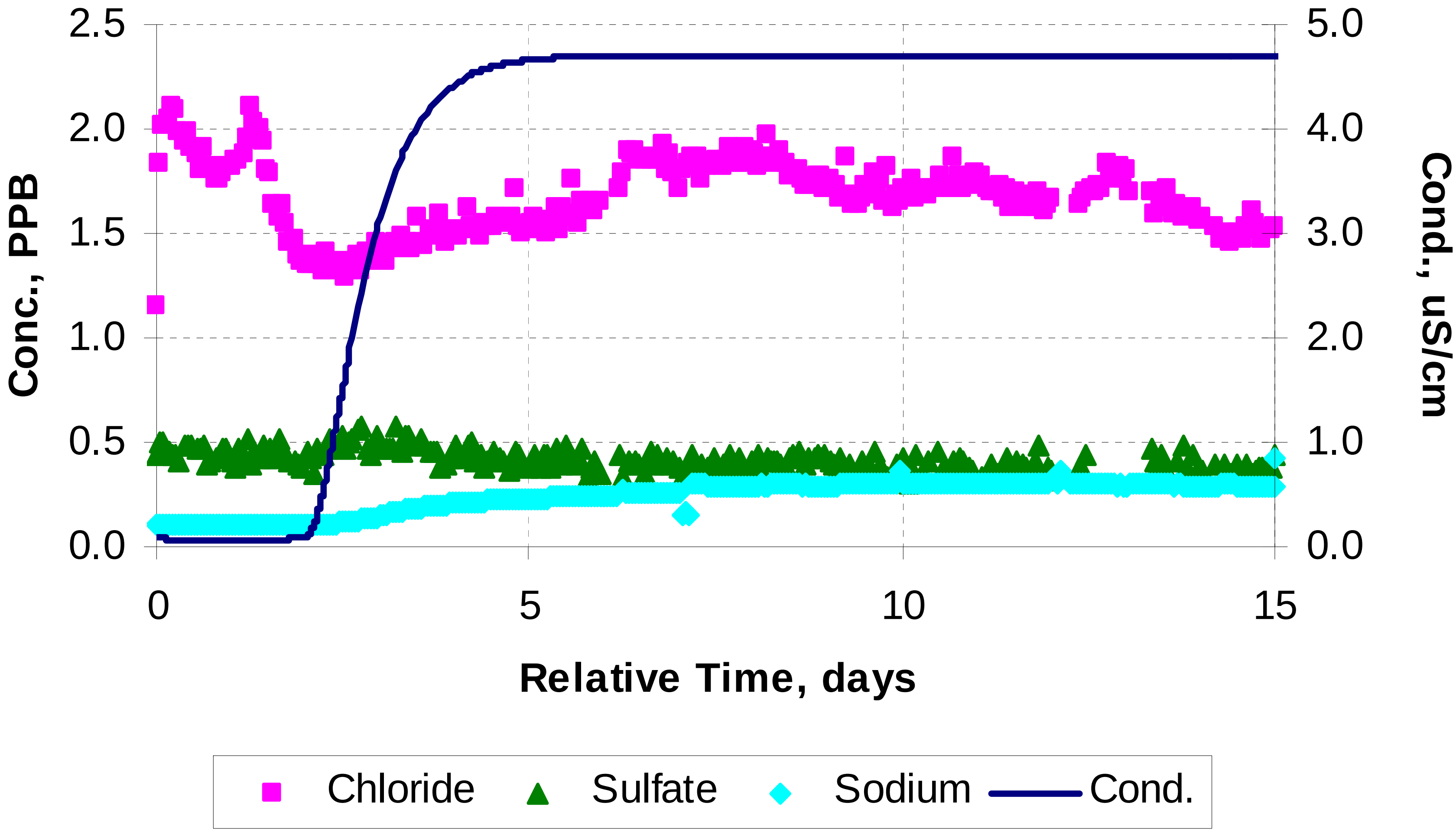
Steam Generator Effects



Millstone Experience

- Ultra Low Chloride Resin Experience
  - >80 Billion Liters of Condensate Processed
  - 5200 Cumulative Service Days
  - 1.2 – 1.4 µg/L Steam Generator Chloride
  - 8 – 15 ng/L Chloride Leakage from Condensate Polishers
  - <u>One</u> Anion Resin Regeneration

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Iron Transport Reduction

- Elevation of ETA Levels
  - Unit 2: ~1.25 mg/L to ~2.75 mg/L
  - Unit 3: ~1.50 mg/L to ~3.50 mg/L
- Reduction in Feedwater Iron Levels
  - Unit 2: ~4.5 µg/L to ~1.6 µg/L
  - Unit 3: ~4.25 µg/L to ~2.0 µg/L

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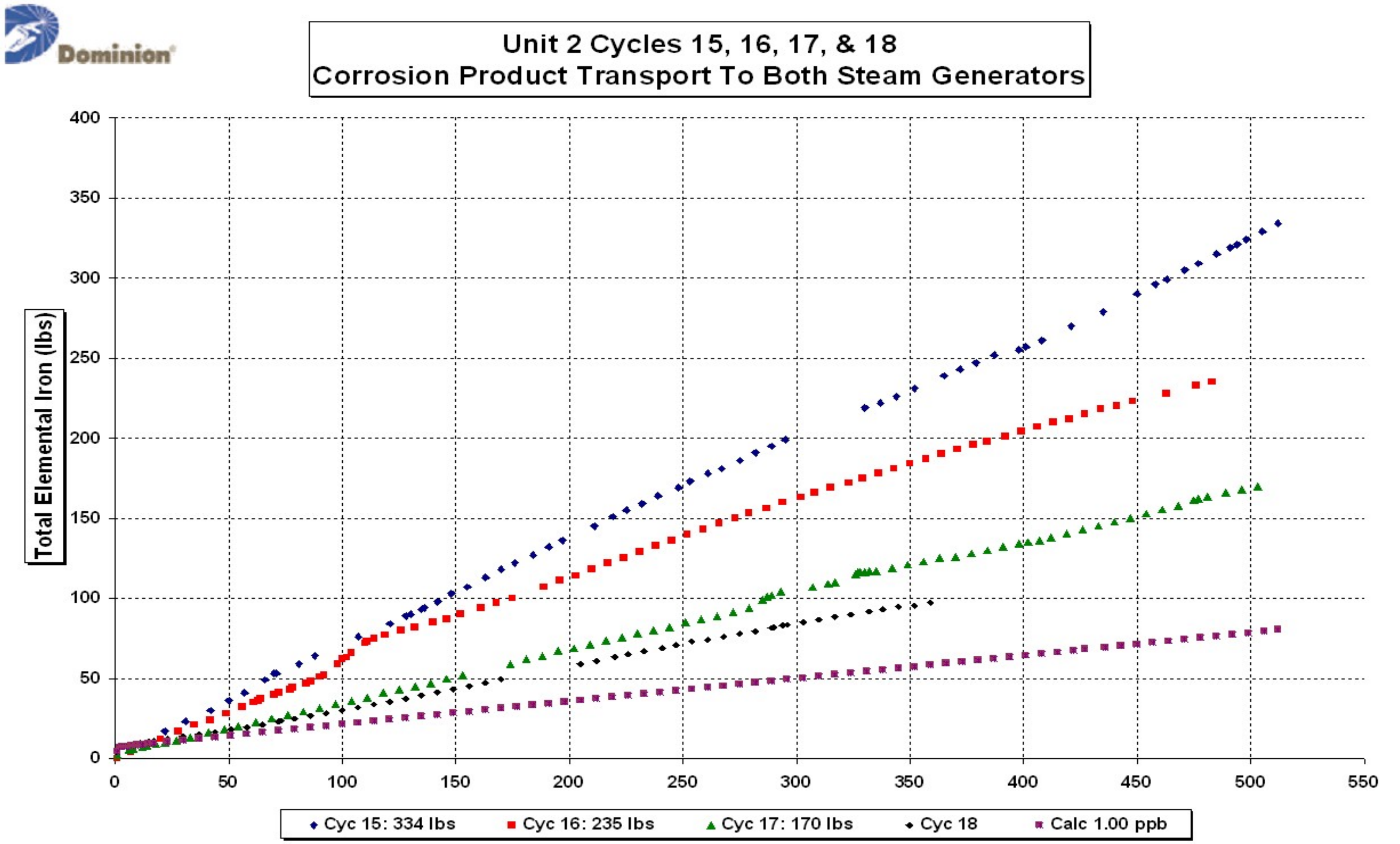
Iron Transport – Unit 2



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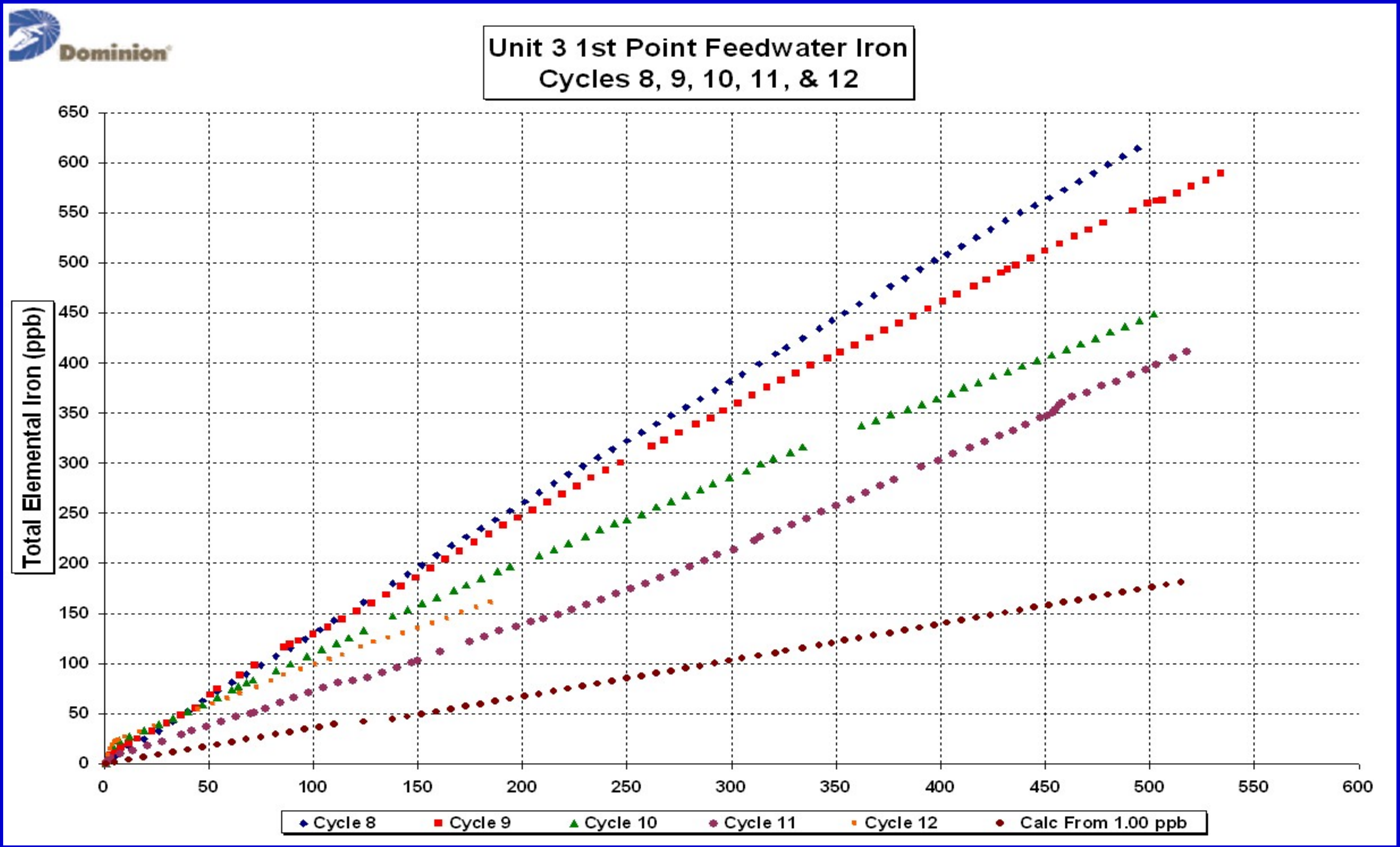
Iron Transport – Unit 3



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Iron Transport Reduction

- Total Iron Reduction
  - Unit 2
    - Cycle 15: >150 kg
    - Cycle 18: <60 kg
    - >60% Decrease
  - Unit 3
    - Cycle 8: >280 kg
    - Cycle 12: <180 kg
    - >35% Decrease

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Conclusions

- Plant Experience with Ultra Low Chloride Resin
  - Mixed Beds in both Units at Millstone Power Station
  - Multiple Lots / Multiple Vessels
  - Extraordinary Service Time (>3.5 years) and Throughput (>21 billion liters)
  - Substantial reduction in ETA cost

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Conclusions

- Plant Experience with Ultra Low Chloride Resin
  - Eliminated Need for On-Site Regenerations of Anion Resin
  - Signicantly Reduced Frequency of Cation Resin Regenerations
  - Allowed On-Line Amination of Cation Resin in Condensate Polishers
  - Successful Operation in Both H/OH and Amine / OH Cycles

Collateral Benefits

- Minimal Chloride Ingress Into Steam Generators
- Reduced Metallurgical Attack in Condensate System and Steam Generator
- Increased Steam Generator Life
- Polisher Operation without Resin Regeneration

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Future Installations

- 2 Units of a PWR
  - Mixed (Deep) Bed Condensate Polishers
  - ETA Chemistry
  - Corrosion Product Reduction
  - Reduce Regeneration Costs
- 1 Unit of a PWR
  - Filter Demineralizers (Powdered Resin)
  - Minimize / Eliminate Chloride Spike Immediately Following Precoating

Ultra Low Sulfate Strong Acid Cation Resins

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Objectives

- Higher Purity Strongly Acidic Cation Resin for Condensate Polishing Applications in BWR's and PWR's
- Reduction in Release of Residual Leachable / Extractable Oligomers ($SO_4^{=}$) from Cation Resin

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Candidate Resins

• Resin A	8% Gellular
• Resin B	10% Gellular
• Resin C	10% Gellular
• Resin D	10% Gellular
• Resin E	10% Gellular
• Resin F	14% Gellular
• Resin G	16% Gellular

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Sulfate Reduction Protocol

- Commercial Cation Resins
- Testing Performed in Plant Scale Equipment
- Subjected to 3 Step Post-Treatment to Reduce Sulfate Extractables / Leachables
- Laboratory Column Extraction
- Ion Chromatography Measurements for Inorganic and Organic Sulfates & Chlorides

Preliminary Results

		Resin A	Resin A	Resin B	Resin B
		Pre-UV $SO_4^{=}$ (ppb)	Post-UV $SO_4^{=}$ (ppb)	Pre-UV $SO_4^{=}$ (ppb)	Post-UV $SO_4^{=}$ (ppb)
As Received		69	103	30	79
1st Post-Treatment		2.3	8.9	4.3	21
2nd Post-Treatment		1.6	8.2	0.35	13
3rd Post-Treatment		1.4	7.5	0.23	16

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Future Work

- Plant Post-Treatment of Resins C, D, E, F, and G
- Aging Studies on all 7 Resins
- Refinement of Ion Chromatography Techniques and Measurements

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Conclusions

- Too Soon To Tell
- Expect to Present Update on this Work at the next EPRI Condensate Polishing Workshop

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